

# **An Integrated Hydrogen Production-CO<sub>2</sub> Capture Process from Fossil Fuel**

## **Semiannual Progress Report**

**Reporting Period Start Date: September 1, 2004**

**Report Period End Date: March 15, 2005**

**Principal Authors: Z. Wang (PI) and K. B. Bota**  
**Clark Atlanta University, Atlanta, GA 30314**  
**Email: [zwang@cau.edu](mailto:zwang@cau.edu) Phone: 404-880-6934**

**D. Day**  
**Scientific Carbons Inc, Blakely, GA**

**Date Report Was Issued: July 2005**

**DOE Award Number: DE-FG26-03NT41914**

**Submitted by: Clark Atlanta University, Atlanta, GA 30314**  
**Eprida Scientific Carbons Inc., Atlanta, GA**

## **DISCLAIMER**

**DISCLAIMER OF LIABILITY:** This report was prepared as accounts of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

**DISCLAIMER OF ENDORSEMENT:** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of document authors herein do not necessarily state or reflect those of the U.S. Government or any state government or any agency thereof.

## **ABSTRACT**

The major project objective is to determine the feasibility of using the char from coal and/or biomass pyrolysis, ammonia and CO<sub>2</sub> emissions at smokestacks to produce clean hydrogen and a sequestered carbon fertilizer. During this work period, literature review has been completed. The project plan, design and test schedules were made on the basis of discussion with partner in experimental issues. Installation of pilot scale units was finished and major units tests were fully performed. Modification of the pyrolyzer, reformer and gas absorption tank have been done. Integration testing is performing recently. Lab scale tests are in operation phase. The experimental installations are discussed in this paper.

## TABLE OF CONTENTS

DECLAMER .....	2
ABSTRACT .....	3
INTRODUCTION AND OBJECTIVES.....	5
EXPERIMENTAL FACILITIES.....	5
RESULTS AND DISCUSSION.....	10
FUTURE PLANS.....	12
SUMMARY AND CONCLUSIONS.....	13
REFERENCES.....	13

## INTRODUCTION AND OBJECTIVES

The increasing anthropogenic CO<sub>2</sub> emissions and possible global warming have challenged the United States and other countries to find new and better ways to meet the world's increasing need for energy while, at the same time, reducing greenhouse gas emissions. The improved technology for integrated hydrogen production/CO<sub>2</sub> capture that we plan to develop through this R&D effort could significantly support President Bush's Global Climate Change Initiative (GCCCI) that commits America to an aggressive strategy to reduce greenhouse gas intensity by 18 percent over the next 10 years. Our new technology concept integrates two significant and complementary hydrogen production and CO<sub>2</sub>-sequestration approaches that have now been developed at Oak Ridge National Laboratory (ORNL) and Clark Atlanta University.

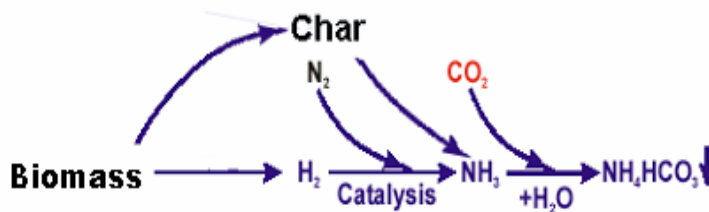


Figure 1 Schematic View of the process from Biomass to Fertilizer

Figure 1 illustrates the schematic view of the process of converting biomass into hydrogen and char. Hydrogen can be efficiently used for stationary power and mobile applications, or it can be synthesized into ammonia, while char can be used for making time-release fertilizers (NH<sub>4</sub>HCO<sub>3</sub>) by absorption of CO<sub>2</sub> and other acid gases from exhaust flows. Fertilizers are then used for the growth of biomass

The objective of the proposed study is to determine the feasibility of using the char from a coal and/or biomass pyrolysis-reforming process and CO<sub>2</sub> emissions at a

smokestack to form a solid  $\text{NH}_4\text{HCO}_3$ -char product that can subsequently be used as a fertilizer. Part of the hydrogen from the pyrolysis-reforming process may be converted to ammonia that is used to solidify the  $\text{CO}_2$  as  $\text{NH}_4\text{HCO}_3$  in the char. The balance of the hydrogen may be purified and sold at market prices or used as a feedstock.

This project plans to perform bench scale experiments and pilot scale tests. The Combustion and Emission Lab at Clark Atlanta University has conducted the bench scale experiments. The facility used for pilot scale tests has built in Athens, GA.

## EXPERIMENTAL FACILITIES

### Part A Hydrogen and char production

Our integrated process consists of two stages: 1) pyrolysis of biomass to generate pyrolysis gas/char, and 2) catalytic steam reforming of pyrolysis gas. Figure 2 shows the schematic flow diagram of the developed process. The flow procedure of the process is as follows: Feeder accepts biomass; the pyrolysis unit pyrolyzes the biomass into pyrolysis gas and char at around  $500^\circ\text{C}$ ; char is leaked out at this stage, while pyrolysis gas flows into baghouse to filter out solid components accompanied with pyrolysis gas; before the gas is introduced into catalytic reformer, the pyrolysis gas is heated up to  $680^\circ\text{C}$ ; in the reformer at  $850^\circ\text{C}$ , most of pyrolysis gas is finally converted into hydrogen, carbon dioxide and water; after condensed and cooled down the water vapor, the mixtures of hydrogen and carbon dioxide, along with the nitrogen and other gases at normal temperature are produced. Hydrogen can be purified from the mixed gases. In our experiments, hydrogen is burned at the exit.

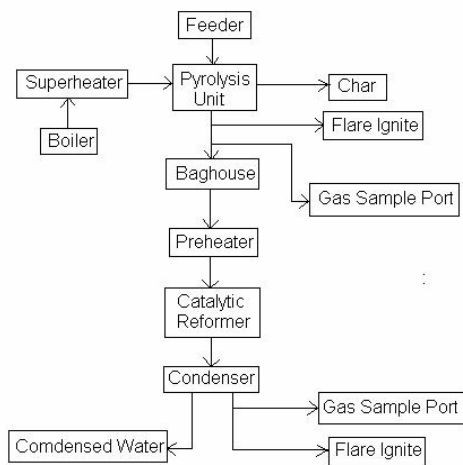


Figure 2 Schematic Flow Diagram of Char and Hydrogen Production

A photo of the pyrolysis unit of the pilot scale plant is shown in Figure 3. Char is led out from bottom of this unit.



Figure 3 Pyrolysis Unit with Biomass feedstock system

## Part B Fertilizer production

The next step after char produced is to make fertilizer. Figure 4 is the Schematic diagram of the bench scale experiments for  $\text{NH}_3$ - $\text{CO}_2$  solidification. Before the  $\text{NH}_3$  and  $\text{CO}_2$

Introduced into the reactor, the char (activated carbon) needs to be mixed with water at various ratios and filled into the reactor. Then, the reactants ( $\text{NH}_3$  and  $\text{CO}_2$ ) flow into the reactor to form a solid  $\text{NH}_4\text{HCO}_3$ -char product that may subsequently be used as a fertilizer. The flow rates of each gas are controlled by MKS flow controllers. The remaining ammonia is absorbed in water bath, while carbon dioxide can be monitored by Agilent Micro GC.

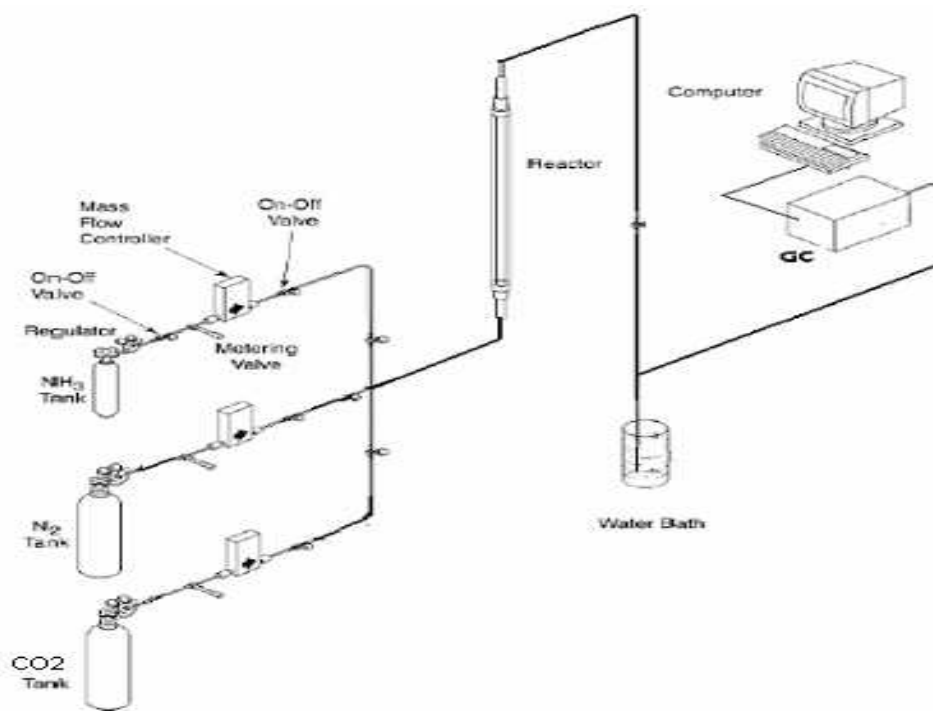


Figure 4 Schematic of Bench Scale Test of  $\text{NH}_3$ - $\text{CO}_2$  solidification



Figure 5 shows the fertilizer reactor for the bench scale experiments. The 1/3 reactor is filled with wet char (20g). After reaction, 3-7 gram of  $\text{NH}_4\text{HCO}_3$  can be formed.



Figure 5 Photo of Bench Scale Test

## RESULTS AND DISCUSSION

The Char and Hydrogen production experiments have been done. Figure 6 illustrates the dry  $\text{N}_2$ -free basis gas composition during a 24-hours operation. It is the final output gas that excludes nitrogen and water. During the 24-hours continuous operation of experiment, 48% (at dry  $\text{N}_2$ -free basis) of hydrogen is obtained from the integration system. Other major components are 35% carbon dioxide, 9% methane and 8% carbon monoxide. Using peanut shells as feedstock, the overall yield from this system is up to 6wt% hydrogen and 32wt% charcoal/activated carbon.

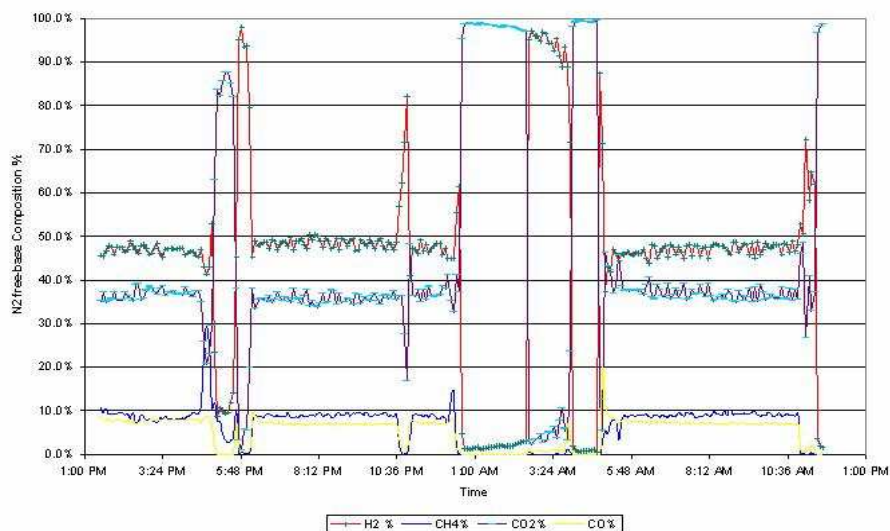


Figure 6 Dry N<sub>2</sub>-free basis gas compositions via Time

The pyrolysis unit has produced char samples, which planned to use as the sequestration material. Figure 7 is the photo of sample char material.

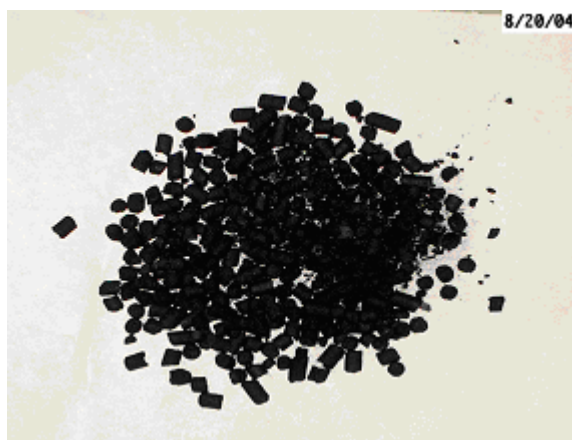


Figure 7 Char material produced by the Pyrolyzer

Figure 8 is the result of investigation of the leaching examination of different chars, which are produced with different exit temperatures, from 400°C-900°C. This figure shows that the 400°C char has the potential of long term slow release of nutrients, hinting good candidate for a time-release fertilizer.

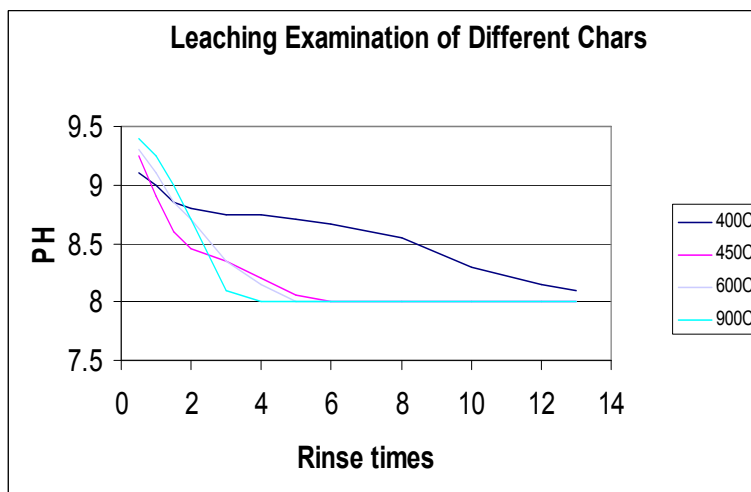


Figure 8 leaching examination of different chars.

Since the char around exit temperature 400°C is good to keep fertilizer time-release. We tested the fertilizer absorption of the char around this temperature (380°C-420°C). Figure 9 shows that the 380°C-420°C chars have similar absorbability and 400°C char is little better.

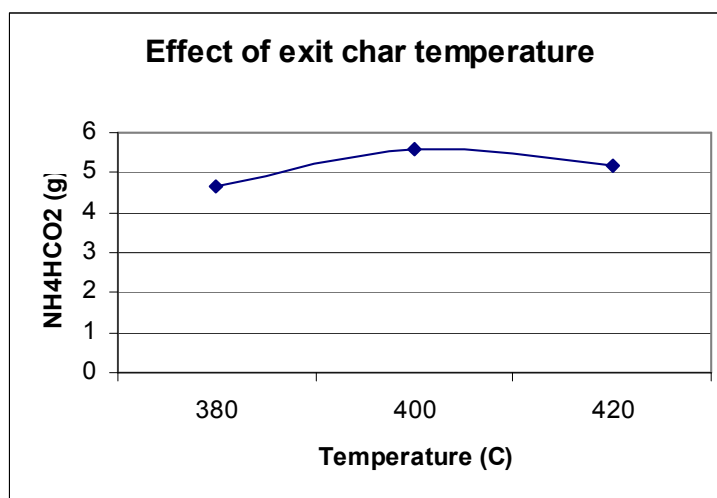


Figure 9 Effect of exit char temperature

Figure 10 illustrates the formation of Ammonium Bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) Char Production.

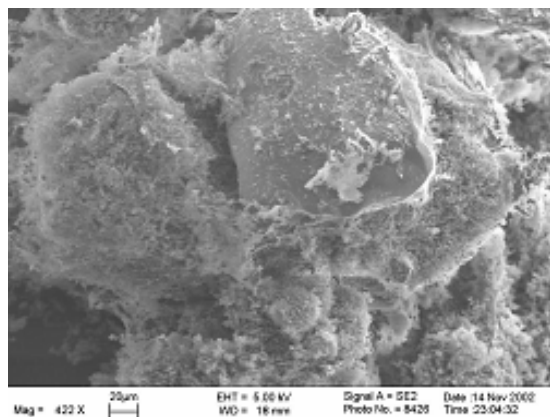


Figure 10 Photo of formation of Ammonium Bicarbonate

## FUTURE PLANS

In the past few months, we have finished the char and hydrogen production experiments, produced char samples, built the setup of bench scale experiments, and initiated the characteristic analysis of char products. The future works include the following tasks.

1. Testing, Analysis and characterization of the char and gaseous products
2. Process optimization
3.  $\text{NH}_3\text{-CO}_2$  solidification process
4. Tests to evaluate fertilizer usage

## CONCLUSIONS

1. The pilot scale hydrogen and char production tests have completed.
2. The bench scale equipment has conducted.
3. The pilot scale facilities are installed and finished char and hydrogen production tests

4. Primary investigation to char characteristics has been conducted.
5. The future works include  $\text{NH}_3\text{-CO}_2$  solidification and tests to evaluate fertilizer usage.

## REFERENCES

1. Lee, J.W.; Li, R. "A Novel Strategy for  $\text{CO}_2$  Sequestration and Clean Air Protection", Proceedings of Fire National Conference on Carbon Sequenstration, Washington,DC, May14-17,2001.[http://www.netl.doe.gov/publication/proceedings/01/carbon\\_seq/p12.pdf](http://www.netl.doe.gov/publication/proceedings/01/carbon_seq/p12.pdf)
2. Lee, J.W.; Li, R. "Method for Reducing  $\text{CO}_2$ , CO,  $\text{NO}_x$ , and  $\text{SO}_x$  Emissions", 1998 ORNL Invention Disclosure, ERID 0631; 2002 U.S. Patent No. US 6,447,437 BI.
3. Lee, J.W.; Li, R (2002). "Integration of Coal-Fire Energy Systems with  $\text{CO}_2$  Sequestration through  $\text{NH}_4\text{HCO}_3$  Production." Energy Convers. Manage, vol. 44, no.9, pg.1451-1464, June 2003.
4. Yelverton, F "The use of activated carbon to inactive agriculture chemical spills", Norh Carolina Cooperative Extension Service, March,1996.  
<http://www.bae.ncsu.edu/bae/programs/extension/publicat/wqwm/ag442.html>
5. Li, E. Hagaman, C. Tsouris, and J.W. Lee (2002). "Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase," Energy & Fuels, 2003, 17(1), 69-74.
6. Miller, D.W., and W.P. Miller, Land application of wastes. P. G217-G241. In M.E. jSummer (ed.) Handbook of Soil Science. CRC Press, Baca Raton, FL.
7. Miller, D.W., and W.P. Miller, S. Dudka, and M.E. Sumner. 2000, Characterization of Industrial By-Products. Soil Sci. Soc. Am., Madision WI.

Oren, R; Ellsworth, D.; Johnsen, K, et.al. (2001) "Soil fertility limits carbon sequestration by forest ecosystems in a CO<sub>2</sub>-enriched atmosphere" Nature 411, 469-472 (24 May, 2001), Letters to Nat